

Ground state and low excited states of the negative hydrogen molecule ion

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With 6 figures in the text

SUMMARY

The potential curves of the lowest states of H_2^- have been calculated in the range of R -values from 1 to 10 a.u. The following states, arranged according to increasing value of the minimum energy, are found to correspond to discrete energy levels: $^2\Sigma_u^+$, $^2\Pi_u$, $^2\Sigma_g^+$, $^2\Sigma_u^+$ and $^4\Sigma_u^+$. The minimum of the potential curve for the ground state is found at $R = 1.65$ a.u. and $E = -1.1057$ a.u., corresponding to a dissociation energy $D_e = 59$ kcal/mole. H_2^- is thus found to be comparatively stable towards dissociation into H and H^- . Moreover, the electron affinity of H_2 is found to be $\text{EA}(\text{H}_2) = -0.28$ eV $= -6.4$ kcal/mole. The bearing of these results on the possible reactions between electrons and H_2 molecules is briefly discussed.

1. Introduction

In a recent discussion of certain dark-structures in the solar corona Öhman [1] has suggested that these structures may be explained as absorption structures, originating from H^- ions. According to Öhman one possibility for the formation of these ions would be by collisions between electrons and H_2 molecules in the ground state, followed by capture of the electrons in formation of H_2^- ions with subsequent dissociation of H_2^- into H and H^- .

Starting from a suggestion by Öhman that inverse predissociation should be important for the recombination of H_2 , the present author [2] has suggested some alternative processes for the formation of H^- by way of H_2^- . For a more detailed study of the transition probabilities in these reactions the potential curves of the ground state and the lowest excited states of H_2^- must be known with some accuracy. The present investigation aims at a theoretical determination of these potential curves.

For a long time the existence of the negative hydrogen molecule ion has been rather questionable, as H_2^- had not been observed in any experiment. However, a recent investigation by Khvostenko and Dukelsky [3] of formation of H^- ions from collisions between electrons and hydrogen molecules indicates that H_2^- ions are possibly formed as an intermediate step in the reaction. Moreover, in a very recent extension of this work [4] the authors claim to have ascertained the appearance in the mass

spectrometer of H_2^- in a yield 20–30 times lower than the yield of H^- . These experiments will be discussed further in connexion with the results of the present investigation.

Previous theoretical investigations of the H_2^- ion by valence bond (VB) methods have been carried out by Eyring, Hirschfelder and Taylor [5] and recently by Dalgarno and McDowell [6]. Eyring *et al.* [5] have studied the lowest state, $^2\Sigma_u^+$, of H_2^- in connexion with an investigation of the ortho-para hydrogen conversion by alpha-particles. By use of a VB treatment with two variation parameters they found that the ground state of H_2^- should be stable, although the formation of the ion should have low probability. They obtained a potential curve with a minimum at an internuclear distance of 1.8 Å, the minimum being 20.9 kcal/mole lower than the potential computed for infinite separation of the nuclei. This limiting value, corresponding to $H + H^-$, was however 37.4 kcal/mole higher than the energy of $H + H + e$, implying that the H^- ion should be unstable in contradiction to the well-known fact that the ground state of H^- is stable, having a dissociation energy of 17.40 kcal/mole [7]. Therefore, the potential curve of H_2^- , computed by Eyring *et al.* [5], is not so well suited for a closer analysis of reactions involving H_2^- ions as well as H_2 molecules and free electrons. For this reason the present investigation is concerned not only with excited states of H_2^- but also with a reexamination of the ground state.

The recent investigation by Dalgarno and McDowell [6], concerned with the ground state and the lowest $^2\Sigma_g^+$ state of H_2^- , is more elaborate than [5]. Still it takes only a single configuration into account. It was published, while the present study was in progress, but unfortunately not noticed by the author until her own calculations were almost completed. Although the present treatment has been carried out independently of [6] the first part of it follows essentially the same lines as [6] and gives almost equivalent results. These results will nevertheless be presented here, because they will be given in a more informative manner and because they are essential for the following part, which takes into account superposition of configurations. A detailed comparison of the methods used in [6] and used here will be given below.

In Section 2 of the present paper an examination of the possible lowest states of H_2^- is given. In Sections 3 and 4 appropriate electronic wave functions for the ground states of H^- and H_2^- are discussed. In Section 5 the wave functions for some of the lowest states of H_2^- are given. Section 6 presents the results of the calculation of the potential curve for the ground state, when a single configuration is used. Section 7 contains the results for the $^2\Sigma_u^+$ states obtained from superposition of configurations. Section 8 contains the corresponding results for the $^2\Sigma_g^+$ states. In Section 9 the results for the $^2\Pi_{u,g}$ states and for the quartets are given. A discussion of the results and of the bearing on the possible reactions between electrons and hydrogen molecules is given in Section 10. The Appendix contains some remarks about the calculations of the pertinent integrals and gives the computed energy values.

2. Classification of the lowest states of H_2^-

In order to find the potential curves of the lowest energy states of the H_2^- ion it is suitable to start from the lowest states of the dissociation products H and H^- . In fact, the large equilibrium distance of H_2^- , found by Eyring *et al.* [5], and the still large distance, found by Dalgarno *et al.* [6], indicates that the states of the molecu-

Table 1. Group-theoretically possible states of H_2^- , resulting from the ground state of H and the lowest states of H^- .

States of separated atoms		States of H_2^-
H	H^-	
$1s^2 S$	$1s^2 \ ^1S$	$2 \sum_{u,g}^+$
$1s^2 S$	$1s \ 2p \ ^3P$	$2,4 \sum_{u,g}^+$
$1s^2 S$	$1s \ 2p \ ^1P$	$2 \sum_{u,g}^+$
$1s^2 S$	$1s \ 2s \ ^3S$	$2,4 \sum_{u,g}^+$
$1s^2 S$	$1s \ 2s \ ^1S$	$2 \sum_{u,g}^+$
		$2,4 \prod_{u,g}$
		$2 \prod_{u,g}$

lar ion should more likely be similar to the states of the separated atoms than to the states of the united atom.

Now, as to H^- , only the ground state has been investigated previously. This state is a $1s^2 \ ^1S$ state. The lowest excited states of heliumlike atoms are $1s2s \ ^3,1S$ and $1s2p \ ^3,1P$. As is well known the energies of the different states of two-electron atoms are approximately proportional to $(Z-s)^2$, where Z is the nuclear charge and s the screening constant. Thus, it can be expected that the lowest excited states of H^- should be very close to the ground state. However, as H^- has a rather small electron detachment energy, it could well be that all excited states of H^- belong to the continuum. Nevertheless, it has been assumed that the lowest states of H_2^- should be derived from the ground state $1s^2 S$ of H combined with the ground state and the lowest excited states of H^- .

The probable sequence of the lowest states of H^- can be obtained in the following way. As is well known from experiments, the energy of the ground state of iso-electronic atoms is to a remarkably good approximation given by the formula

$$E = AZ^2 + BZ + C. \quad (1)$$

In fact, when A , B , C are determined by means of the ground states of He, Li^+ , Be^{+2} , B^{+3} , C^{+4} , it is e.g. found that the ground state energy of H^- should be 16.91 kcal/mole, in excellent agreement with the value 17.40 kcal/mole of Hylleraas *et al.* [7]. Assuming the formula (1) to be valid also for corresponding excited states and by application to the above-mentioned series of atoms it is found that the sequence of the excited H^- states presumably is the one, given in Table 1. It should be mentioned, however, that the accuracy of the values is not good enough to ascertain the actual existence of any discrete excited states of H^- .

The states of the molecular ion H_2^- , which by group-theoretical methods are obtainable from the given atomic states, are also collected in Table 1. It should be remembered, however, that all these states do not necessarily correspond to actual, discrete molecular states, as some of them may belong to the continuum.

3. Ground state of H^-

The ground state of H^- has been thoroughly investigated by several authors. The object of the present study is not to achieve a more accurate value of this ground

state energy. What we are looking for is a wave function, simple enough to be used as a basis for the wave functions of H_2^- but accurate enough to show the stability of H^- .

The simplest wave function for the $1s^2 \ ^1S$ state is

$$\Phi_1 = \text{Det} |\chi_a(\zeta; 1) \bar{\chi}_a(\zeta; 2)|. \quad (2)$$

Here, the notation $\text{Det} |\dots|$ stands for the determinant, having the diagonal term $\dots$. The bar denotes an orbital with negative spin. Absence of the bar implies positive spin. $\chi_a(\zeta; i)$ is an $1s$ atomic orbital (AO) of the electron i at the atom a and with the orbital exponent ζ :

$$\chi_a(\zeta; i) = \sqrt{\frac{\zeta^3}{\pi}} \exp(-\zeta r_{ai}). \quad (3)$$

In the following, the arguments of the AO's will not be written down explicitly, but in any product the arguments of the AO's will always be in the sequence 1, 2, 3, $\dots$

The function (2) was used by Eyring *et al.* [5] for the limit of infinite separation between the nuclei of H_2^- . As mentioned above, they did not obtain stability for H^- by this function, although they treated ζ as a variation parameter. Now, it is well known from the study of heliumlike atoms by e.g. Hylleraas [7] that the computed energy value can be considerably improved by choosing different orbital exponents for the two $1s$ AO's:

$$\Phi_2 = \text{Det} |\chi_a(\zeta) \bar{\chi}_a(\zeta')| + \text{Det} |\chi_a(\zeta') \bar{\chi}_a(\zeta)|. \quad (4)$$

This function has previously been used for H^- by Chandrasekhar [8].

Treating ζ and ζ' as independent variation parameters, he found a value of the energy of H^- , lower than the energy of $H + e$, i.e. H^- is found to be stable. Moreover, he found ζ' to be much smaller than ζ , about $\frac{1}{3}\zeta$. This indicates that the single configuration $1s^2$ does not describe the ^1S state of H^- very well. Consequently, if we had chosen to write the wave function of the ^1S ground state as a superposition of configurations, composed of hydrogen AO's, we would have found a large contribution from the configuration $1s2s$. This conclusion is in agreement with the calculation on He by Taylor and Parr [9]. By inspection of Table 1 it is seen that the ^1S ground state of H^- , as described by the wave function (4), can be interpreted as a superposition of the two configurations in Table 1, which give rise of ^1S states. Obviously, these two configurations will also give rise to an excited ^1S state, orthogonal to the ground state. It can however be predicted that this excited ^1S must have a rather high energy value and thus will not contribute essentially to the lowest Σ states of H_2^- . Consequently, the excited ^1S state will not be considered in the following.

4. Ground state of H_2^-

The H_2^- ion is a system composed of two nuclei a and b , separated by a distance R , and three electrons 1, 2 and 3. We are looking for a comparatively simple eigen-function of the hamiltonian H of this system. As we are interested in the whole potential curve, the VB method should be the most suitable one. According to this method in

its simplest form the unnormalized, electronic wave function of the $2\Sigma_u^+$ ground state is:

$$\Psi_1 = \text{Det}[\chi_a(\zeta)\bar{\chi}_a(\zeta)\chi_b(\zeta)] - \text{Det}[\chi_b(\zeta)\bar{\chi}_b(\zeta)\chi_a(\zeta)], \quad (5)$$

where $\chi(\zeta)$ is the function (3). It is easily seen that in the limit $R = \infty$ Ψ_1 takes the form of Φ_1 , multiplied by the $1s$ function of the free H atom.

It is of some interest to compare the VB function (5) with the function, obtained from the simplest molecular orbital (MO) method. From $1s$ AO's two MO's can be formed:

$$\begin{aligned} \psi_1(\zeta) &= \chi_a(\zeta) + \chi_b(\zeta), \\ \psi_2(\zeta) &= \chi_a(\zeta) - \chi_b(\zeta). \end{aligned} \quad (6)$$

Here ψ_1 is a bonding MO and ψ_2 an anti-bonding MO. If we choose equal orbital exponents of ψ_1 and ψ_2 , the total wave function of the ground state can be written:

$$\Psi_2 = \text{Det}[\bar{\psi}_1\bar{\psi}_1\psi_2] = \text{Det}[(\chi_a + \chi_b)(\bar{\chi}_a + \bar{\chi}_b)(\chi_a - \chi_b)] = -2\Psi_1.$$

Thus, it is seen that, disregarding a numerical factor, which will disappear by proper normalization, the VB method and the MO method in their simplest forms will give the same ground state wave function of H_2^- . This function is also identical with the wave function, used by Eyring *et al.* [5], and with the simplest of the three different functions, used by Dalgarno and McDowell [6].

$$\text{The electronic energy} \quad E = \frac{\int \Psi_1^* H \Psi_1 d\tau}{\int \Psi_1^* \Psi_1 d\tau} \quad (7)$$

is a function of the internuclear distance R and of the orbital exponent ζ . The simplest way of calculating the potential curve is to choose the ζ -value for the free atom and calculate E for different R -values. A refinement can be obtained by variation of ζ for each chosen R -value. This refined calculation has been carried out previously by Eyring *et al.* [5] and by Dalgarno and McDowell [6] but has been repeated by the present author to make possible a detailed comparison of the results of this treatment with the results of alternative calculations..

As has been pointed out above, the limiting function Φ_1 of the function Ψ_1 does not describe the stability of the H^- ion correctly, not even when ζ is varied. To obtain a more correct limiting value of the potential curve we must choose a wave function of H_2^- , which takes the form of Φ_2 in the limit $R = \infty$. This requirement is fulfilled by the following function:

$$\Psi_3 = \varphi_1 - \varphi_2 + \varphi_3 - \varphi_4, \quad (8)$$

where

$$\begin{aligned} \varphi_1 &= \text{Det}[\chi_a(\zeta)\bar{\chi}_a(\zeta')\chi_b(\zeta'')], \\ \varphi_2 &= \text{Det}[\chi_b(\zeta)\bar{\chi}_b(\zeta')\chi_a(\zeta'')], \\ \varphi_3 &= \text{Det}[\chi_a(\zeta')\bar{\chi}_a(\zeta)\chi_b(\zeta'')], \\ \varphi_4 &= \text{Det}[\chi_b(\zeta')\bar{\chi}_b(\zeta)\chi_a(\zeta'')]. \end{aligned} \quad (9)$$

The electronic energy can now be expressed by means of the matrix elements of H ,

$$H_{ik} = \int \varphi_i^* H \varphi_k d\tau, \quad (10)$$

and of the overlap matrix,

$$\Delta_{ik} = \int \varphi_i^* \varphi_k d\tau. \quad (11)$$

The energy will be a function of the four parameters R , ζ , ζ' and ζ'' . To obtain the potential curve the three orbital exponents have been varied independently at each chosen R -value.

The function (8) is equal to the best wave function, used by Dalgarno and McDowell [6]. However, these authors did not vary all the orbital exponents independently. Instead they chose the exponents to be equal to the values, obtained for $R = \infty$, multiplied by a common scale factor ρ , which they varied for each chosen R -value.

5. Lowest excited states of H_2^-

As is shown in Table 1, H_2^- states of the same symmetry can be obtained from several states of the separated atoms. As the states of H^- are expected to lie very close together, it can be anticipated that H_2^- states of equal symmetry will interact considerably.

In principle, wave functions of states with different symmetry could be written down independently, and the variation parameters could be chosen differently. However, in order to keep the computational work within tolerable limits, we have proceeded along the following lines.

From the computation of the potential curve of the ground state we have found that for all R -values the orbital exponents ζ and ζ'' are both almost equal to 1.00. Moreover, the remaining orbital exponent ζ' varies slightly with R but is rather close to 0.30 in the whole interval investigated ($R = 4$ a.u. $-\infty$). Extrapolating this result to the calculation of the excited states, we will not treat the orbital exponents as variation parameters, but give them the values

$$\zeta = \zeta'' = 1.00, \quad \zeta' = 0.30 \quad (12)$$

both for different R -values and for states of different symmetries. Instead of the orbital exponents the variation parameters will be the coefficients of the different configurations, taken into account.

The remaining question is how to choose the orbital exponent ζ''' of the $2p$ AO of H^- . This $2p$ AO should describe the polarization of H^- in the field of the H atom. Obviously, the very diffuse AO $1s(\zeta')$ will be polarized much more easily than the concentrated AO $1s(\zeta)$. Consequently, the $2p$ AO should belong to the set of diffuse AO's, i.e. ζ''' should be

$$\zeta''' = \frac{1}{2}\zeta' = 0.15. \quad (13)$$

The choice (13) should be the best at least for the $2\Sigma_u^+$ ground state of H^- .

Using this value we find the energy of the $1s2p\ ^3P$ state of H^- to be -0.4891 a.u. This value could be compared with the value obtained from extrapolation by aid

of the formula (1). Using the energy values of the $1s2p\ ^3P$ states for the series He, Li^+ , Be^{+2} , ..., tabulated in [10], one obtains for the ^3P state of H^- an energy of -0.4942 a.u., indicating that the value of ζ''' , given by (13), could be used with reasonable confidence.

Prior to listing the configurations of interest we will introduce the following abbreviations:

$$\left. \begin{aligned} s_a &= \sqrt{\zeta^3/\pi} \exp(-\zeta r_a), \\ s'_a &= \sqrt{\zeta'^3/\pi} \exp(-\zeta' r_a), \\ \sigma_a &= \sqrt{\zeta'''^5/\pi} r_a \cos \theta_a \exp(-\zeta''' r_a), \\ \pi_a &= \sqrt{\zeta'''^5/\pi} r_a \sin \theta_a \cos \varphi_a \exp(-\zeta''' r_a). \end{aligned} \right\} \quad (14)$$

Moreover, it will be assumed that the positive lobes of σ_a and σ_b are directed towards each other.

Using the notation (14), the configurations, essentially contributing to the lowest states of H_2^- , can be written:

$$\left. \begin{aligned} \varphi_1 &= \text{Det } |s_a \bar{s}'_a s_b|, & \varphi_4 &= \text{Det } |s'_b \bar{s}_b s_a|, \\ \varphi_2 &= \text{Det } |s_b \bar{s}'_b s_a|, & \varphi_5 &= \text{Det } |s_a s'_a \bar{s}_b|, \\ \varphi_3 &= \text{Det } |s'_a \bar{s}_a s_b|, & \varphi_6 &= \text{Det } |s_b s'_b \bar{s}_a|; \end{aligned} \right\} \quad (15)$$

$$\left. \begin{aligned} \varphi_7 &= \text{Det } |s_a \bar{\sigma}_a s_b|, & \varphi_{10} &= \text{Det } |\sigma_b \bar{s}_b s_a|, \\ \varphi_8 &= \text{Det } |s_b \bar{\sigma}_b s_a|, & \varphi_{11} &= \text{Det } |s_a \sigma_a \bar{s}_b|, \\ \varphi_9 &= \text{Det } |\sigma_a \bar{s}_a s_b|, & \varphi_{12} &= \text{Det } |s_b \sigma_b \bar{s}_a|; \end{aligned} \right\} \quad (16)$$

$$\left. \begin{aligned} \varphi_{13} &= \text{Det } |s_a \bar{\pi}_a s_b|, & \varphi_{16} &= \text{Det } |\pi_b \bar{s}_b s_a|, \\ \varphi_{14} &= \text{Det } |s_b \bar{\pi}_b s_a|, & \varphi_{17} &= \text{Det } |s_a \pi_a \bar{s}_b|, \\ \varphi_{15} &= \text{Det } |\pi_a \bar{s}_a s_b|, & \varphi_{18} &= \text{Det } |s_b \pi_b \bar{s}_a|. \end{aligned} \right\} \quad (17)$$

It is easily seen that $\varphi_1, \varphi_2, \varphi_3, \varphi_4$ of (15) are identical with those obtained from (9) after introduction of (12). In the limit $R = \infty$ these functions are obviously connected with the function (4), describing the ground state ^1S of H^- . $\varphi_1, \varphi_2, \varphi_3, \varphi_4$ will therefore describe the interaction of an H atom with an H^- ion in its stable ^1S state. φ_5 and φ_6 , on the other hand, will describe the interaction of an H atom with an H^- ion in a hypothetical ^3S state. Similarly $\varphi_7, \varphi_8, \varphi_9, \varphi_{10}$ of (16) as well as $\varphi_{13}, \varphi_{14}, \varphi_{15}, \varphi_{16}$ of (17) will describe the interaction of an H atom with an H^- ion in a ^1P state. Finally $\varphi_{11}, \varphi_{12}$ of (16) as well as $\varphi_{17}, \varphi_{18}$ of (17) will describe the interaction of an H atom with an H^- ion in a ^3P state.

To find the correct combinations of these different functions, which actually describe the molecular states of interest, we let the spin operator $\mathbf{S}^2$ operate on the different φ 's. In this way we obtain the following wave functions for the different states of H_2^- :

$${}^2\Sigma_{u,g}^+ \begin{cases} \Psi_3 = \varphi_1 + \varphi_3 \mp (\varphi_2 + \varphi_4), \\ \Psi_4 = \varphi_1 - \varphi_5 \mp (\varphi_2 - \varphi_6), \\ \Psi_5 = \varphi_7 + \varphi_9 \mp (\varphi_8 + \varphi_{10}), \\ \Psi_6 = \varphi_7 - \varphi_{11} \mp (\varphi_8 - \varphi_{12}); \end{cases} \quad (18)$$

$${}^4\Sigma_{u,g}^+ \begin{cases} \Psi_7 = \varphi_1 - \varphi_3 + \varphi_5 \mp (\varphi_2 - \varphi_4 + \varphi_6), \\ \Psi_8 = \varphi_7 - \varphi_9 + \varphi_{11} \mp (\varphi_8 - \varphi_{10} + \varphi_{12}); \end{cases} \quad (19)$$

$${}^2\Pi_{u,g} \begin{cases} \Psi_9 = \varphi_{13} + \varphi_{15} \pm (\varphi_{14} + \varphi_{16}), \\ \Psi_{10} = \varphi_{13} - \varphi_{17} \pm (\varphi_{16} - \varphi_{18}); \end{cases} \quad (20)$$

$${}^4\Pi_{u,g} \begin{cases} \Psi_{11} = \varphi_{13} - \varphi_{15} + \varphi_{17} \pm (\varphi_{14} - \varphi_{16} + \varphi_{18}). \end{cases} \quad (21)$$

Here the upper signs give the u states and the lower signs the g states. It is seen that (18)–(21) will give all the states of Table 1, derivable from the H^- $1S$ ground state and the hypothetical H^- states ${}^3P$, ${}^1P$ and ${}^3S$.

To obtain the best description of the lowest state of each symmetry, linear combinations have been made of all functions of the same kind. As mentioned above, the coefficients in these combinations have been chosen as variation parameters and determined by minimizing the energy.

6. Results for the ground state by use of a single configuration

In this Section we will discuss the results of the calculations on the ground state according to Section 4. The calculations have been carried out in four different approximations:

- I the same value ζ of all orbital exponents, this value being fixed to the value for the free H atom;
- II the same value ζ of all orbital exponents, this value being determined by variation for each internuclear distance;
- III two values ζ' and ζ'' of the orbital exponents, these values being determined by variation for each internuclear distance;
- IV three values ζ , ζ' and ζ'' of the orbital exponents, these values being determined by variation for each internuclear distance.

I and II have been computed by use of the electronic wave function Ψ_1 of (5), and III and IV by use of the wave function Ψ_3 of (8), where in case III we have put $\zeta'' = \zeta$.

II is identical with the treatment of Eyring *et al.* [5] and with one of the cases considered by Dalgarno and McDowell [6]. These authors have also calculated a case identical with the present case I. Case IV is similar to the most accurate treatment in [6], although in [6] all three orbital exponents were assumed to be of the form $\zeta = \zeta_\infty \varrho$, so that only the common parameter ϱ had to be determined by variation for each internuclear distance.

The results of the energy computation are shown in Fig. 1, where the calculated energies E are plotted against the internuclear distance R . The horizontal lines

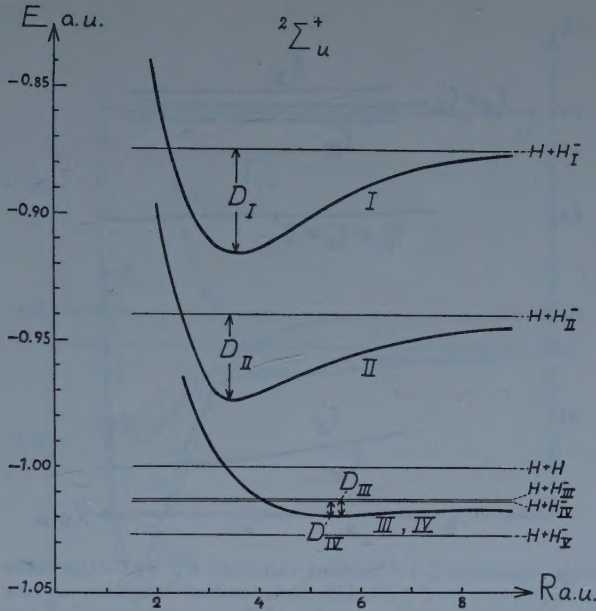


Fig. 1. Potential curves for the ground state $2\Sigma_u^+$ of H_2^- , obtained from the single configuration (8). I: $\zeta \equiv \zeta' \equiv \zeta'' \equiv$ the value for the free H atom. II: Variation of one exponent: $\zeta \equiv \zeta' \equiv \zeta''$. III: Independent variation of two exponents: ζ' and $\zeta \equiv \zeta''$. IV: Independent variation of three exponents: ζ , ζ' and ζ'' . V: Value of $H + H^-$ according to [7]. D = Dissociation energy; the lengths of the vertical arrows show the computed values of D ; the positions of the arrows indicate the computed equilibrium distances.

indicate the energy values at infinite nuclear separation, E_∞ , in the different approximations. The lengths of the vertical arrows, D_I , D_{II} , etc., indicate the computed values of the dissociation energy. The positions of the arrows show the computed equilibrium distances. The pertinent numerical values are listed in Table 2 in the Appendix.

Fig. 1 shows that the computed values of E_∞ are improved in the sequence I, II, III, IV. These values should be compared with the energy level V, which is the sum of the best energy value of H^- , computed by Hylleraas *et al.* [7], and the energy value of the H atom. It is seen that the introduction of *one* variable orbital exponent improves the value of E_∞ by as much as 0.0654 a.u. = 41.1 kcal/mole. The introduction of *two* variable orbital exponents improves this energy value by another amount of 0.0722 a.u. = 45.3 kcal/mole, giving an energy of $H + H^-$ well below the energy -1.00 a.u. of $H + H + e$ in agreement with the well-known stability of H^- . The introduction of *three* independent orbital exponents gives a further improvement of the energy value by only 0.0007 a.u. = 0.4 kcal/mole.

Furthermore, Fig. 1 shows that the values of the computed dissociation energies are in the order $D_I > D_{II} > D_{III} > D_{IV}$. The differences between D_I , D_{II} and D_{III} are considerable. Thus, the potential curve, obtained by use of the simplest wave function, becomes remarkably modified, when the wave function is improved. Moreover, it is seen that D_{IV} is almost equal to D_{III} , indicating that no serious error should be introduced by putting $\zeta \equiv \zeta''$ as has been done in Section 5.

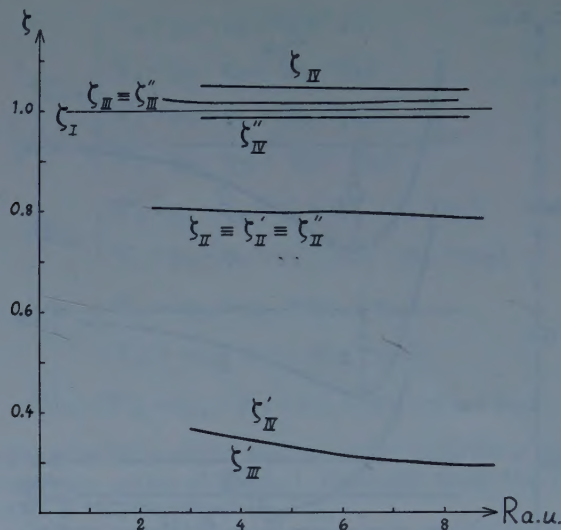


Fig. 2. Values of orbital exponents ζ . I: Constant value of $\zeta \equiv \zeta' \equiv \zeta'' \equiv$ the value for the free atom. II: Variation of one exponent: $\zeta \equiv \zeta' \equiv \zeta''$. III: Independent variation of two exponents: $\zeta \equiv \zeta''$ and ζ' . IV: Independent variation of three exponents: ζ , ζ' and ζ'' .

It should be noted that although the absolute energy values will always be improved when the wave function is improved, this is not at all true for the computed D -value. As long as the value of E_∞ is far from the correct one, the D -value may well diminish drastically, when the wave function is improved.

In Fig. 2 the values of the orbital exponents, obtained in the four different approximations, are shown in terms of R . It is seen that the mean value of ζ , ζ' and ζ'' is about the same for all the three cases II, III and IV. This could be helpful for finding the minimizing values, when more orbital exponents are varied independently.

Curve II of Fig. 1 is the same as that published in [5]. In [6] the authors have only published the energy of interaction between H and H^- , i.e. $E - E_\infty$. At least as far as this difference is concerned the curves I and II of Fig. 1 seem to coincide with the corresponding curves of [6]. Moreover, curve III of Fig. 1 is very nearly the same as the curve obtained from the most accurate treatment in [6], although the two approaches are slightly different. The large excess labour, involved in the present approach IV, apparently does not pay, as it hardly changes the D -value at all.

According to the results given in this Section, the energy of interaction between H and H^- should be of the same magnitude as van der Waals' energies. If these results were conclusive, H_2^- could hardly be considered as a stable molecule and its importance for the formation of H^- , as suggested in [2], would be rather questionable.

7. Results for the ground state and other $^2\Sigma_u^+$ states from superposition of configurations

In this Section the results of the calculations on the $^2\Sigma_u^+$ states according to Section 5 will be presented.

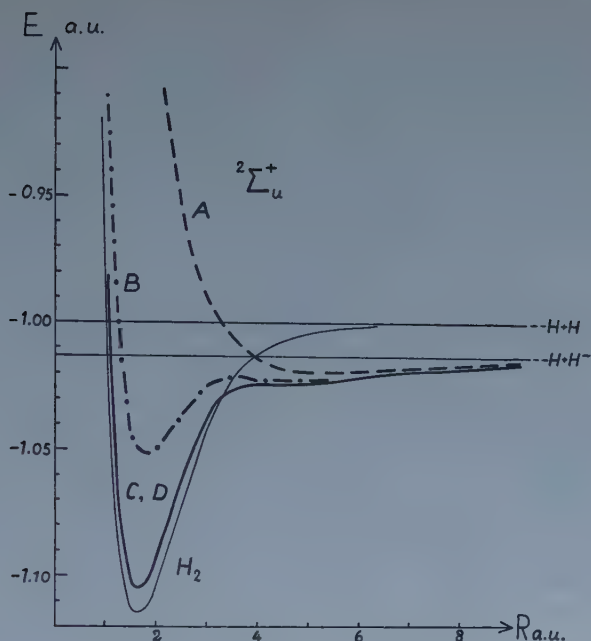


Fig. 3. Potential curves for the ground state $2\Sigma_u^+$ of H_2^- , obtained from superposition of configurations, given in (18). A --- Energy obtained from Ψ_3 , composed of 1s AO's only. B - · - Energy obtained from superposition of Ψ_3 and Ψ_4 , composed of 1s AO's only. C, D — Energy obtained from superposition of Ψ_3 , Ψ_4 , Ψ_5 and Ψ_6 , composed of 1s and 2p AO's. H_2 — Energy of H_2 , computed by the VB method.

The calculations on the ground state have been carried out in four steps by use of an increasing number of the wave functions, given in (18):

- (A) Ψ_3 only;
- (B) superposition of Ψ_3 and Ψ_4 ;
- (C) superposition of Ψ_3 , Ψ_4 and Ψ_6 ;
- (D) superposition of Ψ_3 , Ψ_4 , Ψ_5 and Ψ_6 .

The first step A is almost identical with case III of Section 6, although the constant values (12) of the orbital exponents are used in case A. In Fig. 3 the result of this calculation is given by curve A of dashes. A comparison of this curve with the curve III of Fig. 1, or of the energy values, listed in Tables 2 and 3 in the Appendix, shows that the potential curve A is very nearly the same as the curve III.

The step B consists of a superposition of the functions Ψ_3 and Ψ_4 , both composed of 1s AO's only. This superposition describes the interaction between the $2\Sigma_u^+$ states, derivable from the H^- ground state $1S$ and from a H^- $3S$ state. In Fig. 3 the result of this superposition is given by curve B of dots and dashes. For values of $R > 5$ a.u. the contribution of Ψ_4 to the ground state is almost negligible. At smaller R -values however the superposition changes the potential curve drastically, giving rise to a new and much lower minimum at $R = 1.78$ a.u.

The step C consists of a superposition of Ψ_3 , Ψ_4 and Ψ_6 , describing the interaction between the $2\Sigma_u^+$ states, derivable from the H^- $1S$, $3S$ and $3P$ states. The step D,

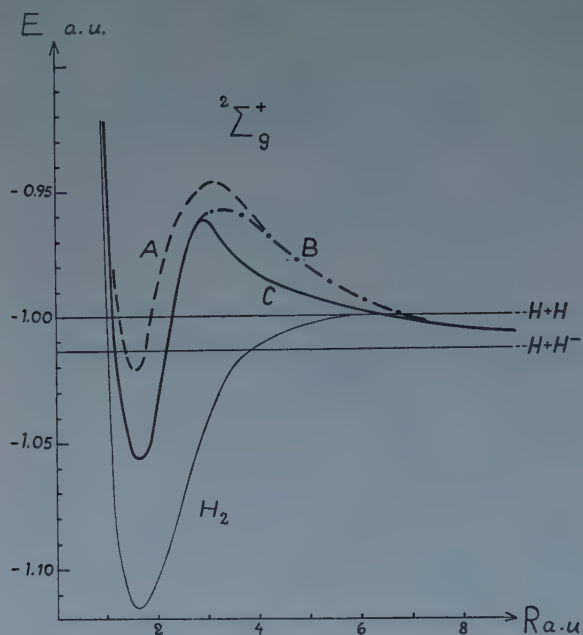


Fig. 4. Potential curves for the lowest $2\Sigma_g^+$ state of H_2^- , obtained from superposition of configurations, given in (18). A --- Energy obtained from Ψ_3 , composed of $1s$ AO's only. B - · - Energy obtained from superposition of Ψ_3 and Ψ_4 , composed of $1s$ AO's only. C ——— Energy obtained from superposition of Ψ_3 , Ψ_4 and Ψ_6 , composed of $1s$ and $2p$ AO's. H_2 ——— Energy of H_2 , computed by the VB method.

finally, consists of a superposition of Ψ_3 , Ψ_4 , Ψ_5 and Ψ_6 , describing the interaction between the $2\Sigma_g^+$ states, derivable from the H^- $1S$, $3S$, $1P$ and $3P$ states. The results of the two last steps are so similar that they are both represented by the thick, solid curve in Fig. 3. The pertinent numerical values are collected in Table 3 of the Appendix. The thin, solid curve in Fig. 3, as well as in Figs. 4, 5 and 6 below, represents the potential curve of the ground state $X^1\Sigma_g^-$ of H_2 and is only given for the sake of comparison. For this reason the curve has been computed by a VB treatment of an accuracy, corresponding to the accuracy of the H_2 calculations, i.e. by use of $1s$ AO's with a constant value 1.00 of the orbital exponent. No $2p$ AO has been included in the H_2 calculation, as the $2p$ AO of H_2^- only has reference to the polarization of the outer, diffuse $1s(\zeta')$ AO.

The inclusion of $2p$ AO's in the wave function for the ground state of H_2 is seen to deepen the minimum considerably and to shift it somewhat towards smaller R -values. The minimum is now found at $R = 1.65$ a.u. and $E = -1.1057$ a.u. It is found to lie very close to the computed minimum of H_2 and only 0.0102 a.u. = 6.4 kcal/mole above this minimum. The D_e -value, computed for H_2^- according to the final step D, is 0.0933 a.u. = 58.6 kcal/mole. Thus, the present calculation shows that H_2^- should be about as stable towards dissociation as molecules in general. On the other hand, the computed value of the electron affinity EA of H_2 is found to be negative, although it has been reduced by a factor ten in comparison to the results of [6]. The value according to step D is $EA(H_2) = -0.28$ eV = -6.4 kcal/mole.

The four different wave functions of ${}^2\Sigma_u^+$ states, given in (18), can, of course, also be used for the computation of potential curves of three excited ${}^2\Sigma_u^+$ states. However, the different wave functions of (18) are not orthogonal, so that the potential curves, obtained from the wave functions Ψ_4 , Ψ_5 , Ψ_6 separately, will have no physical significance. A step, corresponding to step A, can therefore not be used for the calculation of any excited state. On the other hand, in the steps B, C and D one obtains orthogonal, linear combinations of Ψ_3 , Ψ_4 , Ψ_5 and Ψ_6 , two in step B, three in step C and four in step D. In these steps potential curves can therefore be calculated for one, two and three excited states respectively.

The energy values of the three excited ${}^2\Sigma_u^+$ states, obtained from step D, are listed in Table 4 of the Appendix. Two of the states are repulsive. The third excited state has a minimum at $R = 1.73$ a.u. and an energy value of -1.0472 a.u., corresponding to $D_e = 0.0581$ a.u. = 36.5 kcal/mole.

Moreover, it is of some interest to study the coefficients of the different Ψ 's in the linear combinations and their variation with R . It has been found that for R -values of 1–2 a.u. the ground state wave function is essentially composed of the P -functions Ψ_5 and Ψ_6 , whereas the wave function for the attractive, excited state is essentially composed of the S -functions Ψ_3 and Ψ_4 . At R about 3 a.u. there is a strong mixing of different Ψ 's, and at larger R -values the ground state function is essentially composed of Ψ_3 and Ψ_4 and the attractive excited state of Ψ_5 and Ψ_6 .

8. Results for the ${}^2\Sigma_g^+$ states from superposition of configurations

The calculations for the lowest ${}^2\Sigma_g^-$ state have been carried out in several steps, corresponding to the steps A, B and C used in Section 7 for the ${}^2\Sigma_u^+$ ground state. In Fig. 4 the result of step A, i.e. the calculation by use of Ψ_3 only, is given by the curve A of dashes. This curve is repulsive at large R -values, passes a maximum around $R = 3$ a.u. and has a narrow minimum at $R = 1.5$ a.u. The general character of the curve is preserved in the two following steps B and C, although the maximum becomes a little depressed and the minimum is somewhat deepened.

The lowest ${}^2\Sigma_g^+$ state is the only excited state of H_2^+ investigated by Dalgarno and McDowell [6]. Their most accurate treatment of this state is closely related to the present step A. They have only published their results of this treatment for $R \geq 5$ a.u. Within this range of R -values, containing only the repulsive part of the curve, the present results are in good agreement with those given in [6].

The result of step B, describing the interaction between the ${}^2\Sigma_g^+$ states, derivable from the $H^- 1S$ and ${}^3S$ states, where only $1s$ AO's are involved, is given by the curve B of dots and dashes in Fig. 4. At large R -values this curve coincides with the curve for step A, and at small R -values it coincides with the solid curve, representing the result of the following step C. This latter step, consisting of a superposition of Ψ_3 , Ψ_4 and Ψ_6 , describes the interaction between the ${}^2\Sigma_g^+$ states, derivable from the $H^- 1S$, ${}^3S$ and ${}^3P$ states. In this approximation the minimum occurs at $R = 1.54$ a.u. and an energy value of -1.0546 a.u., corresponding to a D_e -value of 0.0422 a.u. = 26.5 kcal/mole.

A step D, in which Ψ_3 , Ψ_4 , Ψ_5 and Ψ_6 are superposed, did not give any sensible result in the case of ${}^2\Sigma_g^+$ states. It is believed that this breakdown of the method depends on the fact that Ψ_5 and Ψ_6 separately give rise to energy values, which for

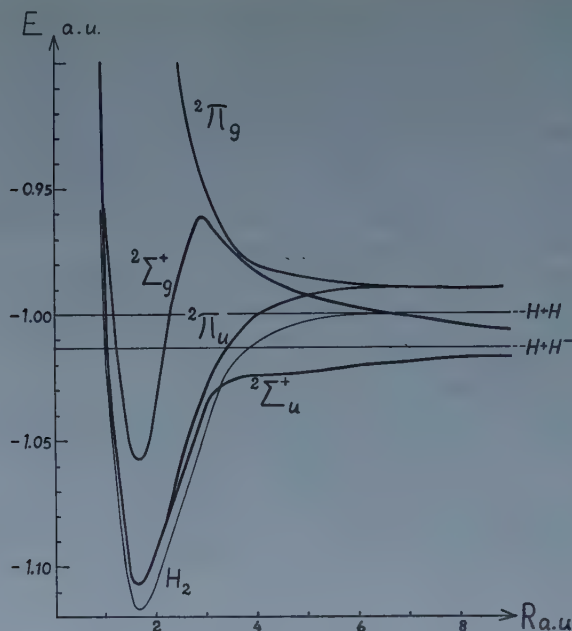


Fig. 5. Potential curves for the lowest ${}^2\Sigma_{u,g}^+$ and ${}^2\Pi_{u,g}$ states of H_2^- together with the curve for the ground state of H_2 .

$R < 3$ a.u. only differ in the fifth decimal place. Now, it is estimated that the energy values are reliable only to the fourth decimal place. Moreover, in the superposition the rather unreliable difference between these two energy values is decisive. It is therefore not surprising that a step D does not work.

As discussed in Section 7, several states of the same species can be calculated by use of the wave functions, given in (18). The final step of the calculation of ${}^2\Sigma_g^-$ states, i.e. the step C, gives thus rise to three different states. The energy values of all three states are listed in Table 5 of the Appendix. The two states, which are not represented in Fig. 4, are both repulsive.

9. Results for the states ${}^2\Pi_{u,g}$, ${}^4\Pi_{u,g}$ and ${}^4\Sigma_{u,g}^+$

The potential curves of the ${}^2\Pi$ states have been calculated partly by use of Ψ_{10}' of (20) and partly from a superposition of Ψ_9 and Ψ_{10}' . The former case describes ${}^2\Pi$ states, derivable from the H^- ${}^3P$ state. The latter case describes the interaction between ${}^2\Pi$ states, derivable from the H^- ${}^1P$ and ${}^3P$ states.

The result for the lowest ${}^2\Pi_u$ state is almost the same with and without superposition of configurations. The discussion of the impossibility of superposing Ψ_5 and Ψ_6 in a step D for the ${}^2\Sigma_g^-$ case applies also to Ψ_9 and Ψ_{10}' in the ${}^2\Pi_g$ case. The energy values of all the ${}^2\Pi$ states are collected in Table 6 of the Appendix. One of the ${}^2\Pi_u$ states is repulsive. The other has a deep minimum at $R = 1.64$ a.u. with an energy

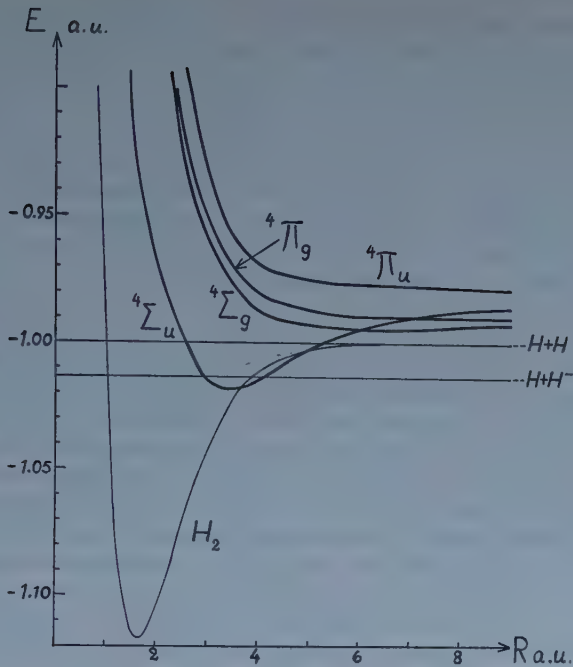


Fig. 6. Potential curves for the lowest $4\Sigma_{u,g}^-$ and $4\Pi_{u,g}^-$ states of H_2^- together with the curve for the ground state of H_2 .

value of -1.1050 a.u., only 0.0007 a.u. above the minimum of the $2\Sigma_u^-$ ground state. The corresponding D_e -value is 0.1159 a.u. $= 72.7$ kcal/mole.

The lowest state in the best approximation of each of the types $2\Sigma_{u,g}^+$ and $2\Pi_{u,g}$ is shown in Fig. 5, together with the computed curve of the H_2 ground state.

The $4\Pi_{u,g}$ potential curves are obtained by use of Ψ_{11} of (21). The computed energy values are listed in Table 7 of the Appendix. Both these states are found to be repulsive.

The $4\Sigma_{u,g}^-$ potential curves are computed in two different approximations: by use of Ψ_7 of (19) and from superposition of Ψ_7 and Ψ_8 . The first case corresponds to the $4\Sigma_{u,g}^+$ states, derivable from the $3S$ state of H^- . The other case describes the interaction between the $4\Sigma_{u,g}^+$ states, derivable from the $3S$ and $3P$ states of H^- . The pertinent energy values are listed in Tables 8 and 9 of the Appendix. In both the Σ_u and the Σ_g case one of the quartets is found to be repulsive. The other $4\Sigma_g^+$ state is found to have a very shallow minimum at $R = 6.7$ a.u. and an energy value of -0.9942 a.u., corresponding to a D_e -value of 0.0051 a.u. $= 3.2$ kcal/mole. Because of this small value, comparable to van der Waals' interaction, and because the whole potential curve of this state is found within the electron detachment continuum according to the present calculations, it cannot be claimed that the existence of this state has been ascertained.

The lowest $4\Sigma_u^+$ state is found to have a minimum at $R = 3.4$ a.u. and an energy value of -1.0164 a.u., corresponding to a D_e -value of 0.0274 a.u. $= 17.2$ kcal/mole. This state seems therefore to correspond to an actual state of the H_2^- molecule.

The lowest states of the species $^4\Sigma_{u,g}^+$ and $^4\Pi_{u,g}$ are reproduced in Fig. 6 together with the computed curve of the H_2 ground state.

10. Discussion of the results

According to the results of the most accurate of the present calculations, presented in Figs. 5 and 6 and in Tables 3–9 of the Appendix several states of the molecule ion H_2^- should be stable towards dissociation into H and H^- . Arranging these states according to increasing value of their energy minima they are $^2\Sigma_u^+$, $^2\Pi_u$, $^2\Sigma_g^+$, $^2\Sigma_u^+$, $^4\Sigma_u^+$.

All the energy minima of the doublets are well below the energy value E_∞ of $H(^2S) + H(^1S)$, which is shown in Figs. 3–6 by the horizontal line, labelled $H + H^-$. It is true that this line shows the value of E_∞ , computed according to Section 3, and is thus somewhat higher than the best known value of E_∞ [7], shown in Fig. 1 by the line $H + H\bar{\nu}$. It is however easily seen that all the energy minima of the doublets are also well below this best value of E_∞ . Therefore, no improvement of the wave functions could diminish the depths of these minima essentially, as did the improvements II, III, IV of the ground state function, summarized in Fig. 1. It seems therefore to be reasonably certain that the states of H_2^- , listed above, actually correspond to discrete electronic energy levels of this molecule ion. However, the list may be incomplete and the given arrangement could be modified by future investigations, because the present calculations are particularly designed to give the best possible value of the ground state energy.

It is interesting to compare this calculated energy level diagram of H_2^- with the corresponding diagram of H_2 . It is seen that the energy levels of H_2^- are very close together, approximately as the triplets of H_2 . This close spacing of the levels of H_2^- depends on the weak bonding of the extra electron, which in the orbital description is expressed by the diffusiveness of the outermost orbital. The close spacing of the energy levels is supposed to be a general feature of negative molecule ions.

The potential curves for all discrete energy levels of H_2^- , calculated by the present author, refer to states obtained from interaction between H in its ground state and H^- in its ground state or in a low-lying excited state. As is seen from Fig. 5 all these curves lie comparatively close to the curve for the ground state of H_2 . Analogously, it may be suggested that states resulting from the interaction between H in an excited state and H^- in low-lying states will give rise to potential curves of H_2^- , lying close to the potential curve of H_2 , having one of the H atoms correspondingly excited. It is true that such hypothetical excited states of H_2^- should belong to the electron detachment continuum. Nevertheless, it is not definitely excluded that they might have a mean life, long enough to allow them to occur as intermediate steps in certain reactions, suggested below.

For the discussion of the reactions, in which H_2^- could possibly participate, it is of interest to know (i) the dissociation energy D_e , discussed above, (ii) the electron affinity of H_2 , $EA(H_2)$, (iii) the energy that must be supplied for vertical detachment of an electron from H_2^- , and (iv) the energy that must be supplied for vertical attachment of an electron to H_2 . The three latter quantities are determined by use of the potential curves for the ground states of both H_2^- and H_2 . Now, the potential curve of H_2^- is only known from the comparatively approximate theoretical calculations in [5] and [6] and in the present paper. As can be inferred from the corresponding

calculations on H_2 , the calculations on H_2^- , performed so far, can by no means give more than a rough estimate of the still unknown experimental potential curve. It seems therefore to be most adequate to compare the calculated potential curve of H_2^- with a potential curve of H_2 , calculated in a corresponding approximation, and not with the experimental potential curve. As discussed in Section 7 above, the potential curve of H_2 that corresponds to most of the treatments of H_2^- , carried out so far, is the curve obtained from the simplest VB treatment, using $1s$ AO's with the constant value 1.00 of the orbital exponents. It is true that the orbital exponents have been varied both in [5] and [6] as well as in the present cases II, III and IV. In view of the similarity between the results of the present cases III and A, the latter with the constant values (12) of the orbital exponents, it seems however to be justified to compare all the different approximations of the potential curve of H_2^- with the above-mentioned H_2 curve. This is also the H_2 curve shown in Figs. 3-6.

From a comparison of this potential curve of H_2 with the potential curve of H_2^- , arising from the present case III, the results of which are very close to the results of the best earlier investigation [6], the following values have been computed: $EA(H_2) = -2.54$ ev = -58.6 kcal/mole; vertical detachment energy of $H_2^- = +0.46$ ev = $+10.7$ kcal/mole; and vertical attachment energy of $H_2 = +8.87$ ev = $+204.6$ kcal/mole. It is seen that these quantities are widely different in the present case III. The same result can probably also be deduced from calculations according to [6].

On the other hand, a comparison of the potential curve of H_2 with the best curve for the ground state of H_2^- , labelled D in Fig. 3, shows that in this case the three above-mentioned quantities have very nearly the same absolute value, the attachment energy being positive and the other two negative, $EA(H_2) = -0.28$ ev = -6.4 kcal/mole.

As has been stressed above, the present theoretical potential curve D of H_2^- is still comparatively far from the correct experimental curve. It seems, however, as if the present result of a negative vertical detachment energy of H_2^- should be correct in view of the fact that He^- has a negative value of this energy, which by use of formula (1) can be estimated to be -0.5 ev. Thus, H_2^- should not be a stable, molecular ion.

By use of the results for H_2^- , discussed at some length above, a tentative explanation of the experimental results of Khvostenko and Dukelsky [3], [4] will now be suggested. According to the first of these papers, [3], the formation of H^- ions from collisions between electrons and hydrogen molecules has been measured as a function of the energy of the electrons. Below 5 ev the yield of H^- ions was negligible. At 7.2 ev a maximum was found, which was attributed to H^- ions, formed by collisions between electrons and water molecules, a low H_2O impurity of the H_2 gas being unavoidable, because apparently H_2O was formed by interaction of H_2 gas molecules and O atoms of the glass wall. Another rather sharp peak was found at 14.5 ev. Finally, after 18 ev it was found that the yield of H^- increased linearly with the electron energy. The authors attributed this last increase to a non-capture collision, followed by dissociation of H_2 into H^+ and H^- . Moreover, they attributed the peak at 14.5 ev to resonance capture of electrons by hydrogen molecules, H_2^- being formed as an intermediate step. This suggestion seems to be confirmed by the later publication [4], according to which the authors obtained not only H^- ions but also a low yield of H_2^- ions in the mass spectrometer, when the experiment was carried out under certain conditions.

These experiments are very difficult to understand in view of the earlier, theoretical investigation of H_2^- [6] and the present case III, predicting a vertical electron attachment energy of H_2 as high as +8.9 eV and a dissociation energy of H_2^- as low as 0.16 eV. The probability of a three-body collision, necessary to stabilize the H_2^- ion, seems to be too low to explain the measured amount of H_2^- .

In view of the best approximation of the present investigation, predicting a vertical attachment energy of H_2 as small as +0.28 eV and a dissociation energy of H_2^- as large as 2.5 eV, it does not seem to be too improbable that an electron could be captured on the collision with a hydrogen molecule, resulting in the formation of an H_2^- ion. The present theoretical results are thus supported by the experiments reported in [3] and [4]. There is however one feature of the experiments, which is not explained by the assumption that the capture collision should give rise to the formation of H_2^- in its ground state, viz. the fact that the formation is only obtained within a rather narrow energy range around 14.5 eV. It is difficult to give an unambiguous explanation of this fact with the present, rather limited knowledge of the possible states of H_2^- . The following is only a tentative attempt.

As is well known, electrons, having an energy within the range 11.8–15.6 eV, will excite H_2 molecules from the ground state to different, excited states, beginning with the triplet state $a^3\Sigma_g^-$. Electrons of an energy somewhat higher than 11.8 eV can therefore excite H_2 either to an excited, vibrational level of this triplet or to any vibrational level of a higher, electronic state. Now, according to the discussion above, it is not unlikely that there are excited energy levels of H_2^- close to the excited states of H_2 . The excited H_2 molecule could therefore possibly capture an electron in transition to an excited H_2^- state. If this is a $^2\Pi_g$ or a $^2\Sigma_g^-$ state, it can radiate in giving the $^2\Sigma_u^+$ ground state of H_2^- . Moreover, if the resulting electronic ground state were vibrationally excited, it might afterwards dissociate, giving H and H^- .

This tentative reaction scheme should also apply to the possible formation of H^- by way of H_2^- in the solar corona [2]. These reactions will, however, be investigated further and discussed more closely in a forthcoming paper.

ACKNOWLEDGEMENTS

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Institute of Theoretical Physics, University of Stockholm, February 1959.

APPENDIX

Computation of integrals

The energy expression from a single configuration, discussed in Section 4, gives rise to integrals, composed of $1s$ AO's only. All these integrals, except the exchange integrals, can be computed by standard methods. In the calculations, including variation of orbital exponents, the exchange integrals were computed by Mulliken's approximation [11].

Superposition of configurations gives rise to integrals over $1s$ and $2p$ AO's. The one-electron two-centre integrals were in this case computed on Besk, using a programme written by Flodmark [12]. The exchange integrals of $1s$ AO's only and with the constant values (12) of the orbital exponents, as well as the hybrid and exchange integrals, containing $2p$ AO's, were obtained by courtesy of Dr. B. Ransil from computation on electronic digital computers, using the programmes written by members of the Laboratory of Molecular Structure and Spectra at the University of Chicago.

Calculated energy values

The energy values of H_2^+ , calculated for different internuclear distances and according to different approximations, are collected in Tables 2-9. Values of internuclear distances R are given in a.u., $1 \text{ a.u.} = 0.52917 \times 10^{-8} \text{ cm}$. Values of total energy E are given in a.u., $1 \text{ a.u.} = 27.2097 \text{ ev} = 627.54 \text{ kcal/mole}$. Dissociation energies $D_e = E_\infty - E$ are given both in a.u. and in kcal/mole.

The values of R and E at the minimum were obtained by fitting a Morse curve to the three nearest points of the $E(R)$ curve. The minimum values are therefore less accurate than the others, but are nevertheless given to the same decimal place in order to facilitate the comparison between the different approximations.

Table 2. Energy values E (a.u.) for different internuclear distances R (a.u.) of the $^2\Sigma_u^+$ ground state of H_2 according to the four cases, I, II, III, IV, discussed in Section 6.

R	Energy values E of H_2^+ according to case			
	I	II	III	IV
2.0	-0.8528	-0.9120	—	—
3.0	-0.9108	-0.9709	—	—
4.0	-0.9134	-0.9719	-1.0141	-1.0143
5.0	—	—	—	-1.0191
5.3	—	—	—	-1.0192
6.0	-0.8899	-0.9550	-1.0185	-1.0190
8.0	-0.8794	-0.9464	-1.0167	-1.0173
10.0	-0.8758	-0.9421	-1.0150	-1.0159
∞	-0.8750	-0.9404	-1.0126	-1.0133
Minimum:				
R (a.u.)	3.55	3.47	5.72	5.42
E (a.u.)	-0.9152	-0.9743	-1.0185	-1.0192
D_e (a.u.)	0.0402	0.0339	0.0059	0.0059
D_e (kcal/mole)	25.2	21.3	3.7	3.7

Table 3. Energy values E (a.u.) for different internuclear distances R (a.u.) of the $^2\Sigma_u^+$ ground state of H_2^- from superposition of configurations according to the four cases A, B, C, D, discussed in Section 7.

For comparison the energy values E of the H_2 ground state from the simplest VB method are given in the last column.

R	Energy values E of H_2^- according to case				E of H_2 from simplest VB method
	A	B	C	D	
1.0	-0.3567	-0.9106	-0.9831	-0.9851	-0.9964
1.5	-0.7291	-1.0434	-1.1011	-1.1023	-1.1127
2.0	-0.8848	-1.0491	-1.0919	-1.0938	-1.1035
3.0	-0.9903	-1.0244	-1.0343	-1.0362	-1.0417
4.0	-1.0139	-1.0222	-1.0225	-1.0238	-1.0113
6.0	-1.0183	-1.0197	-1.0197	-1.0209	-1.0005
8.0	-1.0166	-1.0169	-1.0169	-1.0179	-1.0000
10.0	-1.0150	-1.0151	—	—	-1.0000
∞	-1.0124	-1.0124	-1.0124	-1.0124	-1.0000
Minimum:					
R (a.u.)	5.76	1.78	1.64	1.65	1.64
E (a.u.)	-1.0184	-1.0518	-1.1043	-1.1057	-1.1159
D_e (a.u.)	0.0060	0.0394	0.0919	0.0933	0.1159
D_e (kcal/mole)	3.8	24.7	57.7	58.6	72.7

Table 4. Energy values E (a.u.) for different internuclear distances R (a.u.) of the three excited $^2\Sigma_u^+$ states (1), (2), (3) of H_2^- , obtained from superposition of configurations according to the case D, discussed in Section 7.

R	Energy values E of H_2^- for state		
	(1)	(2)	(3)
1.0	-0.8990	-0.2518	+2.5901
1.5	-1.0386	-0.6813	-0.4134
2.0	-1.0402	-0.8439	-0.6829
3.0	-1.0134	-0.9314	-0.8382
4.0	-0.9981	-0.9413	-0.8660
6.0	-0.9904	-0.9539	-0.8696
8.0	-0.9903	-0.9621	-0.8748
∞	-0.9891	-0.9888	-0.9217
Minimum:			
R (a.u.)	1.73	—	—
E (a.u.)	-1.0472	—	—
D_e (a.u.)	0.0581	—	—
D_e (kcal/mole)	36.5	—	—

Table 5. Energy values E (a.u.) for different internuclear distances R (a.u.) of the three $^2\Sigma_g^+$ states (1), (2), (3), of H_2^- , obtained from superposition of configurations according to the cases A, B, C, discussed in Section 8.

R	Energy values E of H_2^-				
	For the lowest $^2\Sigma_g^+$ state (1), according to case			According to case C for the higher $^2\Sigma_g^+$ states	
	A	B	C	(2)	(3)
1.0	-0.9431	-0.9549	-0.9551	-0.2942	-0.1603
1.5	-1.0216	-1.0537	-1.0543	-0.6727	-0.5518
2.0	-0.9875	-1.0316	-1.0323	-0.8369	-0.7381
3.0	-0.9470	-0.9606	-0.9619	-0.9519	-0.8840
4.0	-0.9629	-0.9637	-0.9831	-0.9583	-0.9027
6.0	-0.9932	-0.9943	-0.9969	-0.9845	-0.8984
8.0	-1.0041	-1.0044	-1.0048	-0.9879	-0.9069
10.0	-1.0081	-1.0081	—	—	—
∞	-1.0124	-1.0124	-1.0124	-0.9891	-0.9217
Minimum:					
R (a.u.)	1.5	1.54	1.54	—	—
E (a.u.)	-1.0216	-1.0540	-1.0546	—	—
D_e (a.u.)	0.0092	0.0416	0.0422	—	—
D_e (kcal/mole)	5.8	26.1	26.5	—	—

Table 6. Energy values E (a.u.) for different internuclear distances R (a.u.) of the two $^2\Pi_u$ states and the $^2\Pi_g$ state of H_2^- , discussed in Section 9.

R	Energy values E of H_2^- for			
	Lowest $^2\Pi_u$ state from Ψ_{10}	$^2\Pi_u$ states from superposition of Ψ_9 and Ψ_{10}		Lowest $^2\Pi_g$ state from Ψ_{10}
		Lowest state	Higher state	
1.0	-0.9827	-0.9849	+ 3.4408	-0.2913
1.5	-1.1006	-1.1018	-0.5828	-0.6713
2.0	-1.0908	-1.0927	-0.8112	-0.8358
3.0	-1.0287	-1.0306	-0.9347	-0.9518
4.0	-0.9991	-1.0005	-0.9652	-0.9803
6.0	-0.9887	-0.9901	-0.9757	-0.9888
8.0	-0.9880	-0.9898	-0.9776	-0.9893
∞	-0.9891	-0.9891	-0.9888	-0.9891
Minimum:				
R (a.u.)	1.64	1.64	—	—
E (a.u.)	-1.1036	-1.1050	—	—
D_e (a.u.)	0.1145	0.1159	—	—
D_e (kcal/mole)	71.9	72.7	—	—

Table 7. Energy values E (a.u.) for different internuclear distances R (a.u.) of the $^4\Pi_u$ state and the $^4\Pi_g$ state of H_2^- , discussed in Section 9.

R	Energy values E of H_2^- for	
	$^4\Pi_u$ state	$^4\Pi_g$ state
1.0	+ 3.4382	- 0.2887
1.5	- 0.5837	- 0.6706
2.0	- 0.8376	- 0.8354
3.0	- 0.9326	- 0.9520
4.0	- 0.9692	- 0.9806
6.0	- 0.9770	- 0.9893
8.0	- 0.9782	- 0.9898
∞	- 0.9891	- 0.9891

Table 8. Energy values E (a.u.) for different internuclear distances R (a.u.) of the two $^4\Sigma_u^+$ states of H_2^- , discussed in Section 9.

R	Energy values E of H_2^- for		
	Lowest state from Ψ_7	States from super- position of Ψ_7 and Ψ_8	
		Lowest state	Higher state
1.0	- 0.2657	- 0.2845	+ 1.9993
2.0	- 0.7905	- 0.9688	- 0.7694
3.0	- 0.8897	- 1.0145	- 0.8830
4.0	- 0.9085	- 1.0139	- 0.9067
6.0	- 0.9176	- 0.9943	- 0.9176
8.0	- 0.9263	- 0.9857	- 0.9251
∞	- 0.9217	- 0.9891	- 0.9217
Minimum:			
R (a.u.)	—	3.4	—
E (a.u.)	—	- 1.0164	—
D_e (a.u.)	—	0.0274	—
D_e (kcal/mole)	—	17.2	—

Table 9. Energy values E (a.u.) for different internuclear distances R (a.u.) of the two $^4\Sigma_g^+$ states of H_2^- , discussed in Section 9.

R	Energy values E of H_2^- for		
	Lowest state from Ψ_7	States from superposition of Ψ_7 and Ψ_8	
		Lowest state	Higher state
1.0	-0.1395	-0.3357	-0.1387
2.0	-0.7045	-0.8463	-0.6902
3.0	-0.8403	-0.9596	-0.8248
4.0	-0.8760	-0.9871	-0.8592
6.0	-0.8850	-0.9939	-0.8637
8.0	-0.8861	-0.9937	-0.8635
∞	-0.9217	-0.9891	-0.9217
Minimum:			
R (a.u.)	—	6.7	—
E (a.u.)	—	-0.9942	—
D_e (a.u.)	—	0.0051	—
D_e (kcal/mole)	—	3.2	—

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